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14. ABSTRACT. The main goal of this project was to develop new lithographic and nanofabrication approaches for the assembly of novel nanoelectronic and nanomagnetic device structures. Our team's interests, expertise and facilities spanned materials synthesis, nanoscale characterization, nanoscale lithography and processing, and involved three institutions (University of Virginia, Notre Dame University, Lund University). To fabricate annular structures of giant magnetoresistive material for proposed vertical magnetic random access memory structures, we explored use of a novel negative inorganic resist, HSQ. Using electron and ion beam exposure of the resist (as well as direct focused ion beam sputtering of the GMR material) we were able to create structures at or close to the project goal of 75/225 nm internal/external annular diameter. It was found that electron beam exposure offered slightly higher resolution but substantially lower throughput than ion beam exposure of the resist. The resultant exposed HSQ patterns offered good etch masks for physical sputtering of the underlying GMR material, an important consideration given the known challenges in reactive ion etching of these materials. Other studies focused on ultra-rapid sputtering of PMMA using focused ion beams and exploring fabrication of inexpensive masks for electron projection lithography. We also explored nanoscale processing and contacting of nanowire structures with our collaborators at Lund University, with application to proposed quantum dot architectures such as quantum cellular automata.

15. SUBJECT TERMS
Nanolithography, Magnetic memory, Nanowire, Electron beam lithography, Focused ion beam

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FINAL REPORT

N000140211039, Fabrication of NanoScaled Systems

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Project Goals: The main goal of this project was to develop new lithographic and nanofabrication approaches to the assembly of novel nanoelectronic and nanomagnetic device structures. To realize this goal, we assembled a team whose interests, expertise and facilities spanned materials synthesis, nanoscale characterization, nanoscale lithography and processing of nanostructures, spanning three institutions (University of Virginia, Notre Dame University, Lund University) The application vehicles for our work were vertical giant magnetoresistive structures for ultra-high density magnetic random access memory (V-MRAM), and prototype III-V semiconductor architectures for quantum cellular automata (QCA) structures.

Advances in Nanoscale Lithography: In developing new nanoscale lithographic methods, the primary metrics were: i) Resolution, ii) Throughput, iii) Adaptability to the device architectures studied.

Our most substantial body of work was upon the application of a novel negative inorganic resist material, hydrogen silsesquioxane (HSQ). This material was employed because of its potential as both a high resolution resist and as an effective etch mask. Magnetic materials such as Ni, Fe, Co, and Cu are particularly difficult to pattern at high resolutions because of the difficulty in dry etching because of the lack of volatile etch products. Our work showed that it was possible to overcome these difficulties using HSQ. HSQ was patterned using both electron beam lithography and a Ga^+ ion focused ion beam, followed by an argon plasma etch. Using these methods, we were able to fabricate ring structures as small as 60/150 nm, Figure 1 (internal/external dimensions of the annulus) in the HSQ, with transfer into underlying GMR materials at dimensions close to project goals of 75/225 nm internal/external diameter, e.g. Figure 2 (we were also able to pattern 75/195 nm structures into underlying Si substrates). The best resolution obtained for e-beam processing of HSQ was c. 30 nm line width. The electron beam sensitivity of the HSQ resist for optimal exposure was found to be relatively low; of order 500 $\mu C/cm^2$. In comparison, we also explored ion beam exposure of the HSQ. This was substantially more rapid, with optimal doses of order 10-20 $\mu C/cm^2$, i.e. 1-2 orders more rapid than e-beam exposure. However, feature definition was not as good as for e-beam exposure. While we could still obtain linewidths of order 30-40 nm in the HSQ, the feature edges were substantially rougher for ion beam exposure, and for annular patterns for vertical MRAM, we obtained rather irregular features for external diameters much below 300 nm, Figure 3. We also employed direct ion beam sputtering of the MRAM structures, yielding structures close to our 75/225 nm OD/ID target, Figure 4. This is a process which requires no resist or subsequent processing steps, but is considerably slower as a typical sputter yield of say 3 atoms per incident ion would imply an equivalent dose of 10,000 $\mu C/cm^2$ for sputtering 40 nm into the film surface. There is also the issue of whether the direct implantation of the energetic (30 keV) Ga^+ ions into the periphery of the patterned GMR rings will cause degradation of the magnetoresistive properties of this structure.

In summary of this work, we found that electron beam exposure of HSQ provided s spatial resolution at or very close to our target of 75/225 nm annular structures, and provided adequate etch resistance for subsequent pattern transfer into the GMR structure (next section of

this report). This is achieved at patterning rates a factor of about 5x slower than conventional PMMA resists (resist sensitivity of c. 500 $\mu C/cm^2$ for HSQ vs c. 100 $\mu C/cm^2$ for PMMA),but the PMMA would not provide nearly such as an effective mask for pattern transfer by sputtering. Ion beam exposure of the HSQ is much more rapid, with exposure doses 10-20 $\mu C/cm^2$, but has spatial resolution limited to about 300 nm OD. There also issues with the ion range in the resist: If the range is less than the resist thickness, then it can be difficult to remove the entire resist, while if it is greater than the resist thickness then some direct implantation into the GMR structures will occur. (We note that a current project at UVa to develop a mass-selecting FIB column will ameliorate this problem, as a far wider range of ion sources will be available, and a choice of primary ion that does not degrade GMR properties will be possible). Finally direct FIB patterning (via sputtering) can provide structures with the required dimensions, but with the likelihood of degraded GMR properties. This particular method offers opportunities for rapid structural prototyping, as no resist or subsequent processing steps are required, but standard Ga^+ FIB sputtering is likely limited to creation of test structures for e.g. development of subsequent pattern transfer procedures. Development of new sources using our mass-selecting may extend this application.

Other activities under this project addressed scaling of lithographic patterning. In one activity, we built upon a discovery in a previous DARPA (Molecular Level Printing) program that direct exposure of PMMA resist to 30 keV Ga^+ ions produces an extraordinarily high sputter yield, up to c. 10^3 sputtered atoms per incident ion, Figure 5a. Under ONR funding, we have substantially extended our understanding of the mechanism and limits of this process. Examination of the dependence of sputtering rate upon PMMA chain length showed that the sputtering rate increases with chain length, which is the signature of an ion-induced unzipping reaction. For sputtering of mean molecular weight chains of 495,000 amu, observed sputtering rates as high as 10^4 were observed (a 10-fold increase over our previous observations of 50k amu PMMA), Figure 5b. This corresponds to an effective dose as low as a few $\mu C/cm^2$ for sputtering of a 50 nm resist film. Comparison to observed sputtering rates in other polymeric materials (e.g. polystyrene and AZ and SU8 resists), coupled with time of flight SIMS measurements indicate that the relevant mechanism is indeed ion induced chain unzipping in conjunction with chain scission mechanisms. While this mechanism does not offer obvious advantages for patterning of the annular GMR structures described above, it does offer a fascinating potential route to PMMA processing generally, particularly if coupled to more technologically compatible ion sources (e.g. a Si beam for processing of Si)! It also offers a route to high throughput master manufacturing for micro-contact printing.

The highest throughput lithography mechanism worked on in this project is a unique projection electron beam lithography system at UVa, SCALPEL (which followed Lloyd Harriott from Bell Labs). While this instrument offers a viable route to wafer level patterning (and featured on the SIA semiconductor roadmap for a while), it generally requires extensive investment in "start up costs" as a projection mask needs to be fabricated, typically costing several tens of thousands of dollars. In this work (also funded by Selete and Sematech) we used FIB Pt deposition patterns on both C film (c. 20 nm thick) TEM samples) and silicon nitride membranes on Si substrates to create ultra-low cost projection masks, Figure 6, with 120 nm features on the "projection mask", which would correspond to 30 nm features on the final sample. This work suggests a route to combining a high throughput production tool with a far more adaptable, low cost mask scheme for research applications.

Vertical MRAM Structures: As discussed in the previous section, electron beam exposure of HSQ enabled annular patterns in the resist as small as 60/150 nm internal/external diameter. A recognized problem in patterning of GMR structures is the difficulty of reactive ion etching because of the lack of volatile etch products. In our work we therefore used physical argon ion sputtering to transfer the pattern from the resist into the underlying GMR. The great advantage of the HSQ is that being as an inorganic material that is relatively dense after exposure and developing, it is relatively sputter resistant. In practice, we observed relative sputter ratios of approximately unity between GMR substrate and resist (for both electron and ion exposed HSQ), which we would not expect to be attainable using polymeric resists. This sputter ratio enabled us to sputter through the depth of the GMR material while maintaining the HSQ mask, for HSQ thicknesses that were sufficiently thin (50 – 100 nm) to allow high resolution patterning. We realized dimensions at or very close to project goals of 75/225 nm for the annular GMR structures, e.g. Figure 2.

GMR structures, and simpler test structures of component metals, were fabricated using the new biased target ion beam deposition system at UVa. A typical fabricated GMR structure is shown in Figure 7. Following resist and GMR patterning, as described above, preliminary GMR measurements were made on individual as-fabricated annular structures using a Zyvex S100 nano-manipulator under observation in the FIB or SEM. We found it impractical to make good measurements of vertical transport through the GMR rings, due to the difficulty in locating probes with the necessary tens of nm precision without deforming the probe tip, so measurements across the GMR ring were made using local contact pads, Fig. 8. The observed resistance with applied magnetic field was very variable between measurements, although for some measurements resistance variations of several percent over field variations of several hundred Oe were observed. More measurements are needed to understand and accurately quantify this response.

Nanowire / QCA Structures: In collaboration with colleagues at Lund University (Lars Samuelson, Lars Montelius, Jonas Johanson, Sara Nilsson), we are developing new methods for processing and manipulation of semiconductor nanowires. In particular, as developed in a visit to Lund by project PIs Robert Hull and Greg Snider in discussion with Lars Samuelson, we are examining this architecture as a potential route to fabrication off QCA structures, Figure 9. A key requirement to realize this structure is the ability to be able to make contact at different heights of the quantum wire. We are developing two approaches to this task: (i) Using spun polymers to create platforms for contact lines at different heights, and (ii) Using FIB deposition to create local SiO_2 spacers to bring in FIB deposited contact lines at the correct height., Figure 9. Approach (i) is illustrated in Figure 10 where planar layer of a low-k dielectric material, benzocyclobutene (BCB) is spun onto the nanowire sample, followed by an anisotropic etch in a CF_4 plasma to expose the tips of the nanowires. Approach (ii) is illustrated in Fig 11, however it is noticeable that there is some bending of the nanowires in the vicinity of the deposited contacts. The amount of bowing is a function of the stiffness / elastic constants of the wires - it is pronounced for InAs nanowires, but minimal for GaP nanowires, for example. The phenomenon is illustrated even more clearly in Fig. 12, which shows cross-sectional (TEM) and plan view (FIB secondary electron) images of wires near an SiO_2 deposit. The presence of a film coating the internal (with respect to the position of the SiO_2 deposit) face of the wire is pronounced. We are currently confirming the nature of this film, but assume that it is related to the organic precursor (TEOS) of the SiO_2 deposit. We are also developing methods for local doping of nanowires using the mass-selecting FIB instrument described previously. Another effort has

been on the FIB fabrication of nano/micro cantilevers and beams, with a goal of understanding nanoscale elastic properties of one dimensional structures, as well as for sensing applications. In combination, we intend that these techniques will give us additional degrees of freedom in local processing of nanowires, leading to the potential for new device architectures such as QCAs.

Publications and Presentations:

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- R. Hull, Y. Liu, D. Longo, W-K Lei and M. Reed, "FIB Fabrication of topographic masters for nanoprinting techniques " (Invited) Int Conf. on Nanoimprint and Nanoprint Technology, San Francisco, Dec 2002
- R. Hull, Y. Liu, M. Kammler, S. Atha, D. Longo and F.M. Ross "Nanofabrication with Focused Ion Beams" (Invited) Scanning Microscopy International, Washington DC, May 2003
- L.R. Harriott and R. Hull, "Nanolithography" in "Introduction to Nanoscale Science and Technology", Springer, 2004. (Unfortunately, acknowledgement not included in published article).
- R. Hull, Y. Liu, S. Atha, A. Portavoce, M. Kammler, D. Longo and F.M. Ross "Nanofabrication with Focused Ion Beams" (invited) RMS-Nano, London, Aug 2004
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- C. Chen, M. Cabral, , L.R. Harriott and R. Hull, "Fabrication of Vertical GMR Structures with Electron Beam Lithography and Focused Ion Beam Lithography", Electron Ion Photon Beam and Nantoechnology (EIPBN) Symposium. Presentation, May 2006
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- Gregory L. Snider, Vishwanath Joshi, Robin A. Joyce, Aaron A. Prager, Hubert George , Alexei O. Orlov, Craig S. Lent, and Gary H. Bernstein, "Quantum-dot Cellular Automata, Experimental Implementations," The Sixth international Conference on Low Dimensional Structures and Devices, April 2007.
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- C.C. Wu, Y. Liu and R. Hull, "Nanoscale thermal analysis of thin films under focused ion beam irradiation via the finite element method", in revision (2007)
- S. Ghatnekar-Nilsson, J. Graham, R. Hull and L. Montelius, "Multi-Frequency Response from a Designed Array of Nanomechnical Cantilevers using a Focused Ion Beam", Nanotechnology 17, 5233-7 (2006)

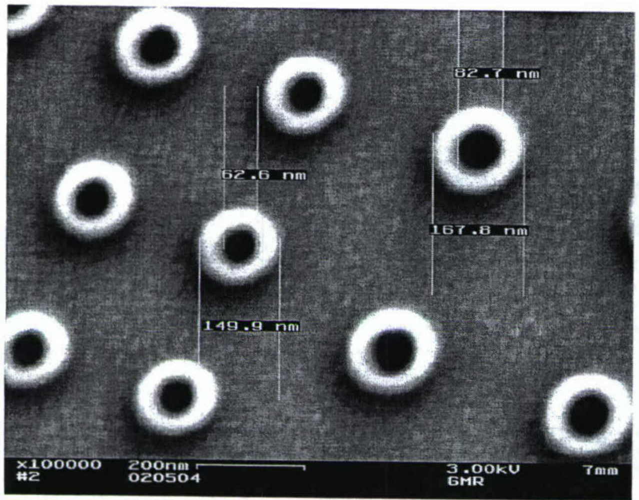

Figure 1: 60 / 150 nm internal / external diameter annuli created by electron beam exposure of HSQ

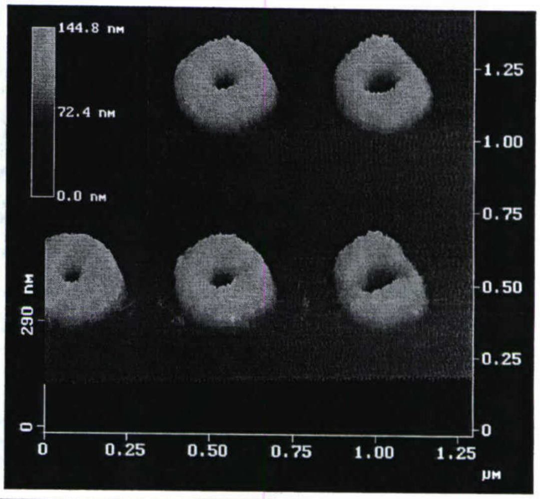

Figure 2: c. 80 / 240 nm internal / external diameter annuli patterned into GMR metal stacks

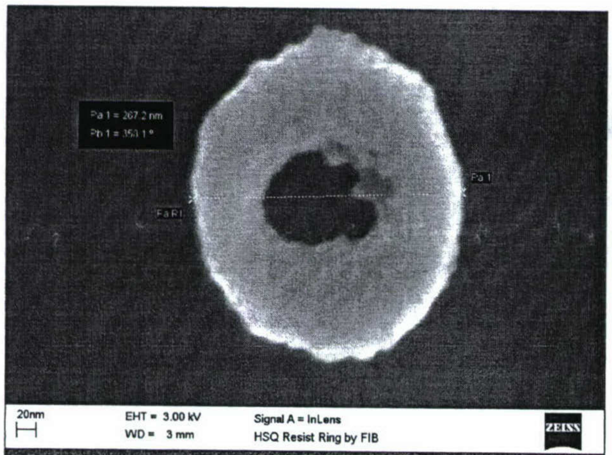

Figure 3: 80 / 270 nm internal / external diameter annuli created by ion beam exposure of HSQ at 18 $\mu C/cm^2$

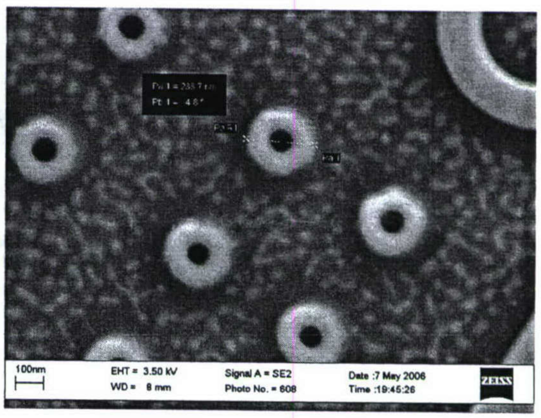

Figure 4: 80 / 240 nm internal / external diameter annuli created by direct FIB sputtering of GMR structures

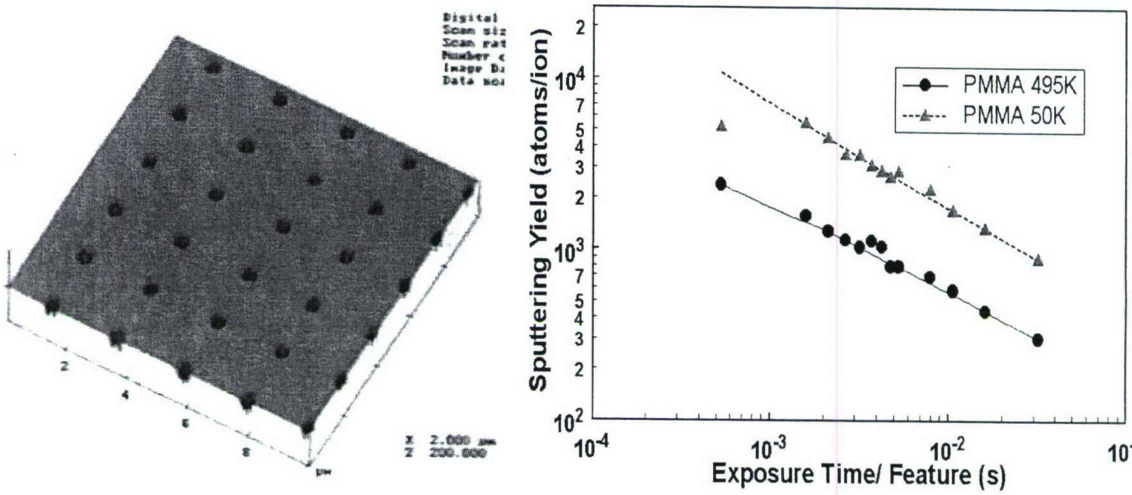

Figure 5: Left – AFM image of 50k PMMA exposed to 1 pA, 100 μs pulses. Right – comparison of sputter rates vs. depth for 50k and 495k PMMa

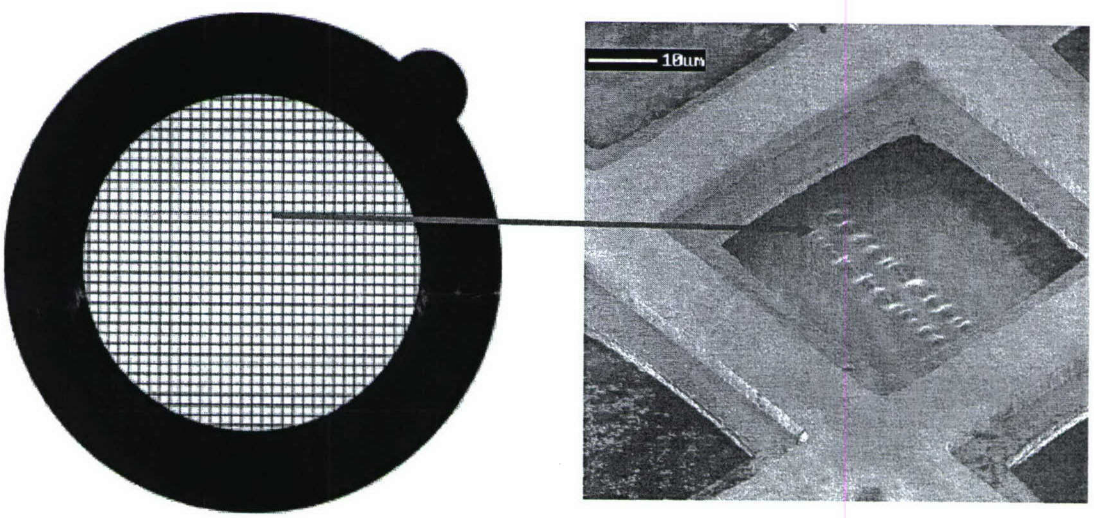

Figure 6: FIB deposition of Pt patterns on a 20 nm thick C film TEM sample as a prototype electron beam projection mask

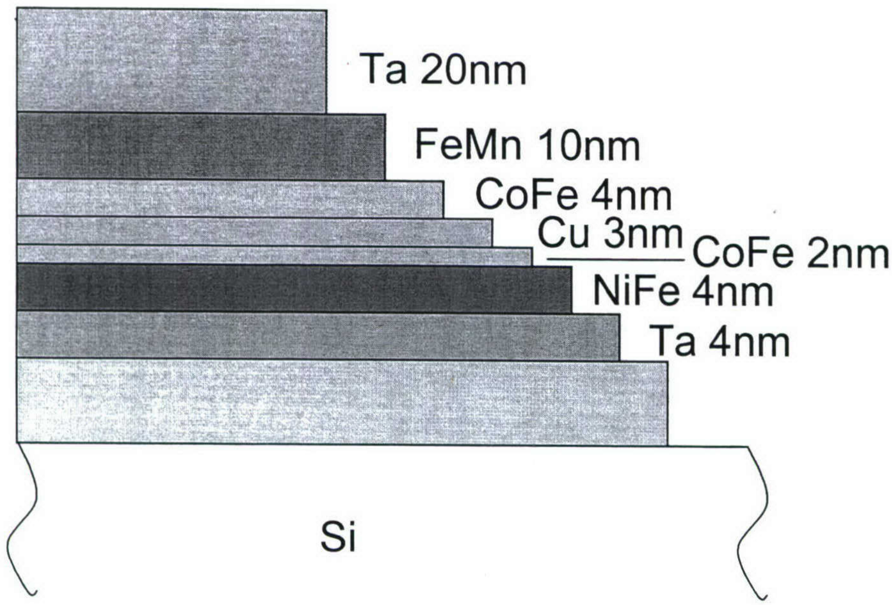

Figure 7: typical GMR structure grown using the biased target ion beam deposition system at UVa

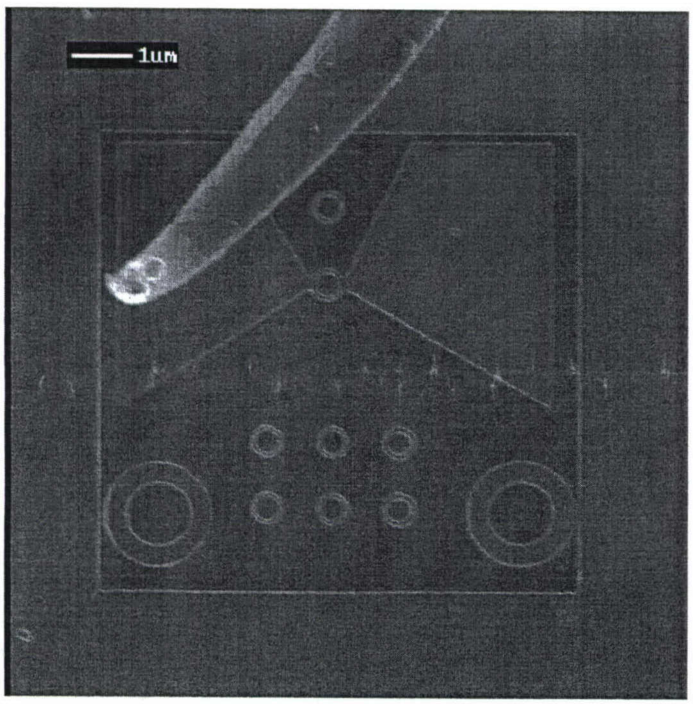

Figure 8: Illustration of experimental measurement of magneto-resistance of individual annular GMR structures vs. applied field

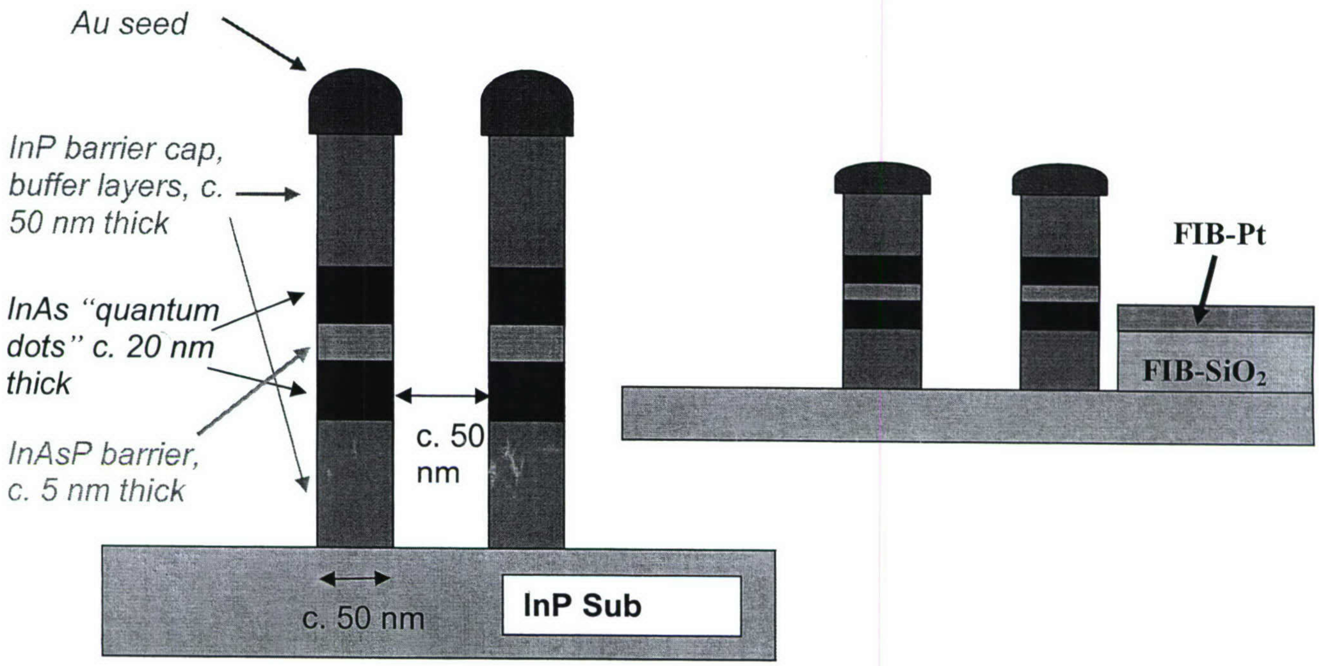

Figure 9: Left - schematic illustration of nanowire based QCA architecture. Right – schematic illustration of FIB contacting

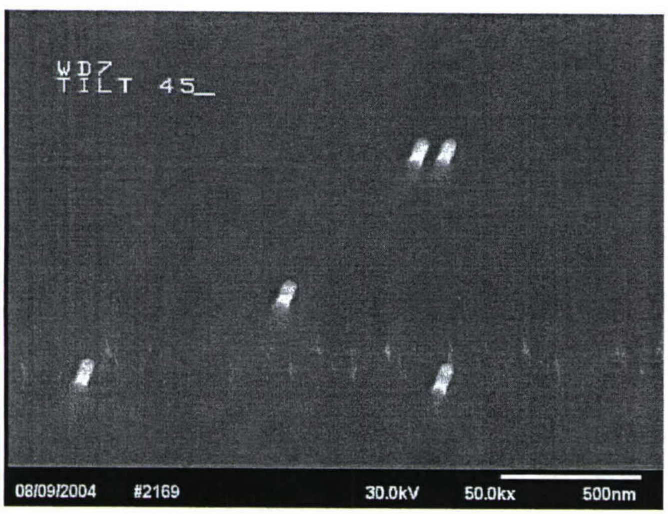

Figure 10: Tips of nanowires protruding from the spun BCB layer

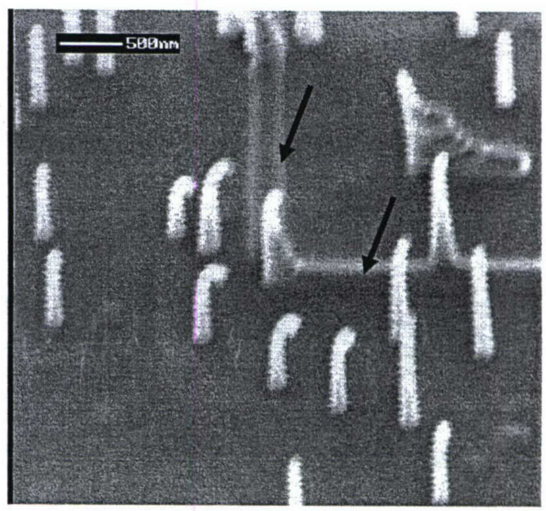

Figure 11: FIB deposited contacts (arrowed) to nanowires

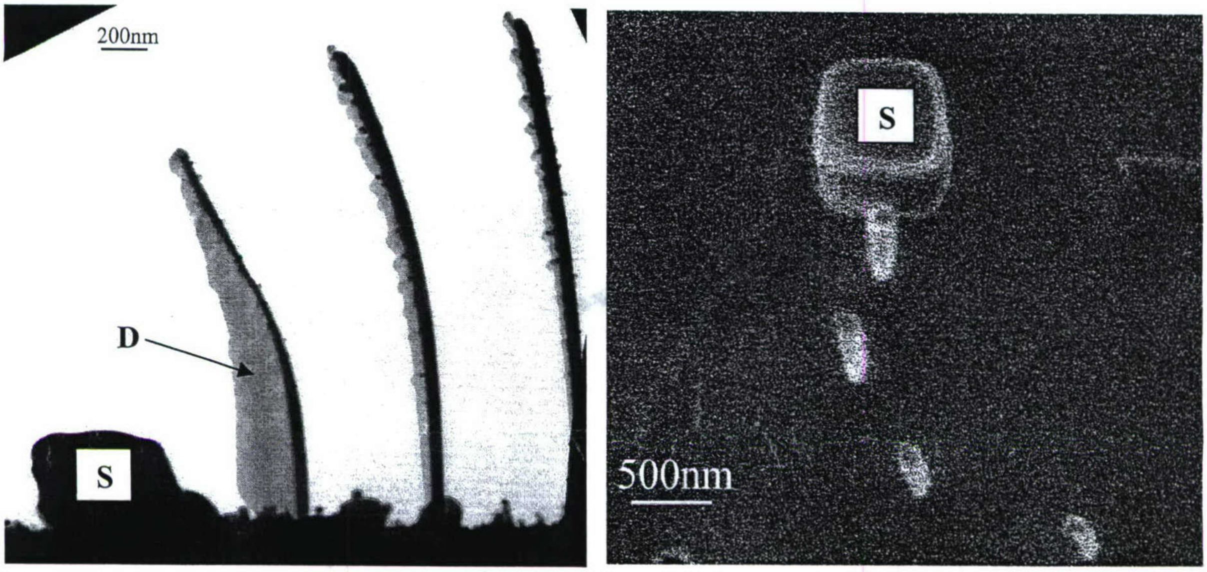

Figure 12: Cross-sectional TEM image (left) and top view FIB secondary electron image of nanowires near an SiO_2 deposit (S). The nature of the deposit D on the interior faces of the nanowires is under investigation